APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2006; **20**: 521–526
Published online 29 June 2006 in Wiley InterScience
(www.interscience.wiley.com) DOI:10.1002/aoc.1081

Synthesis and catalytic activity of binuclear $Mn^{(III,III)}$–BINOL complexes for epoxidation of olefins

Mitesh J. Patel and Bhavna M. Trivedi*

Department of Chemistry, Faculty of Science, M. S. University of Baroda, Vadodara 390 002, Gujarat, India

Received 13 October 2006; Revised 6 March 2006; Accepted 27 March 2006

The novel binuclear complexes $[Mn_2^{(III,III)}(BINOL)_3L_2]2H_2O$, where, L = 2,2′-bipyridine (Bpy) or 1,10-phenanthroline (Phen) and BINOL = 1,1′-bi-2-naphthol were synthesized and characterized by elemental analyses, magnetic susceptibility and various spectral methods. The catalytic activity of these complexes was studied for the epoxidation reaction of unfunctionalized olefins like styrene, 1-hexene, 1-octene and 1-decene. The products thus obtained were analyzed by GC. The epoxidation reactions were carried out, in the presence of catalyst with different oxidants, to study the effect of the nature of the oxidant on the reactions. The different oxidants used were the peroxide oxygen donor (e.g. TBHP and H_2O_2), mono oxygen donor (e.g. PhIO) and dioxygen donor (e.g. molecular O_2). TBHP was found to be the best oxidant for the epoxidation reaction. To study the effect of the solvent on the epoxidation, the reactions were carried out in different media, such as a polar media (e.g. with CH_3OH as solvent), non-polar media (e.g. with CH_2Cl_2 and C_6H_6 as solvents) and coordinating solvent (e.g. CH_3CN). The maximum epoxide formation was observed in CH_2Cl_2 medium. The epoxidation reactions with optically active BINOL catalysts under optimum established conditions were carried out to examine the enantioselectivity of the catalysts. The complexes were, however, found not to be enantioselective. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: *R*-(+)-/*S*-(−)–BINOL; C_2-symmetry axial chiral ligand; binuclear $Mn^{(III,III)}$–BINOL complex; Mn-bipyridine/Phenanthroline complex; epoxidation; oxidation of olefins

INTRODUCTION

Asymmetric epoxidation of prochiral alkenes presents a powerful strategy for the synthesis of enantiomerically enriched epoxides, which are important intermediates for the formation pharmaceuticals and agrochemicals.[1–3] For this purpose, various metal complexes with chiral ligands have been employed.[4–14] The chiral BINOL ligand, which is identified as a versatile chiral reagent, has been used extensively for developing catalytic or stoichiometric methods of enantioselective epoxidation.[4] Recently, Shibasaki *et al*. have used lanthanum or ytterbium complexes with modified BINOL derivatives as catalysts in the asymmetric epoxidation of enones using *t*-butyl hydroperoxide (TBHP) as oxidant.[11–14]

*Correspondence to: Bhavna M. Trivedi, Department of Chemistry, faculty of Science, M. S. University of Baroda, Vadodara 390 002, Gujarat, India.
E-mail: trivedibhavna@yahoo.com
Contract/grant sponsor: M.S. University.

Metal complexes of BINOL, with manganese ion, are not known, although a number of metal complexes of BINOL with lanthanides have been reported.[11–14] Hence, in the present paper, we report the synthesis of binuclear $Mn^{(III,III)}$ complexes with optically active BINOL. The complexes were synthesized by reaction of BINOL [*R*-(+)-, *S*-(−)- or racemic] and 2,2′-bipyridine or 1,10-phenanthroline with the metal salt, $Mn(OAc)_2{\cdot}2H_2O$. These complexes were then characterized by elemental analysis, magnetic susceptibility and various spectral techniques including UV–visible, IR, CD and FAB mass spectroscopy. The catalytic activity of these complexes was measured by studying selected epoxidation reactions. The studies were carried out by changing various parameters like solvent (CH_2Cl_2, CH_3OH, CH_3CN and C_6H_6), oxidant (TBHP, H_2O_2, molecular O_2 and PhIO) and substrate (styrene, 1-hexene, 1-octene and 1-decene). The complexes with optically active BINOL were used as catalysts for the enantioselective epoxidation of styrene.

EXPERIMENTAL

Materials

All solvents were purchased from Qualigens and purified by methods given in Vogel's Practical Organic Chemistry.[15] Methanol was distilled from magnesium turnings and iodine. Dichloromethane was washed with sulfuric acid, sodium carbonate solution (5% in water) and water, dried over solid calcium carbonate and finally distilled prior to use. Acetonitrile was distilled from calcium hydride. Benzene was distilled from sodium wire. β-Naphthol, $FeCl_3$ and $Mn(OAc)_2{\cdot}2H_2O$ were purchased from S. D. Fine and used as received. Cinchonidine, benzyl chloride, 2, 2′-bipyridine, 1,10-phenanthroline, TBHP (70% solution in water) and H_2O_2 (40% solution in water) were purchased from Merck and used as received. Iodobenzene, 1-hexene, 1-octene and 1-decene were purchased from Lancaster and used as received. Styrene was purchased from Fluka and used as received.

Physical measurements

Elemental analyses

All elemental analyses were carried out on a Perkin Elmer CHN 2400 Analyzer, by decomposing the substance (ligand and complexes) at high temperature and estimating the combustion products by TCD. The system was calibrated using acetonitrile supplied by Perkin Elmer prior to use.

Electronic spectra

All UV-Visible spectra were recorded on a Perkin Elmer Lamda-35 in the range 200–800 nm, using 0.001 M solutions of complexes in CH_2Cl_2 and CH_2Cl_2 as references.

IR spectra

All FTIR spectra were recorded on a Perkin Elmer Spectrum RX1 spectrometer in the range 4000–400 cm^{-1}. The samples were taken in KBr pellet form, prepared by mixing the samples with dried IR spectroscopic grade KBr (supplied by Merck) in 1 : 100 w/w ratio with a hydraulic press. The instrument was calibrated using polystyrene film, supplied by Perkin Elmer prior to use.

Magnetic study

The magnetic study of the complex was carried out using Gouy's method using a Mettler balance with an electromagnet of capacity 3000 Gauss. The set up was calibrated using $Hg[Co(CNS)_4]$ prior to use. The tube filled with complex was weighed without external magnetic field and then in presence of external magnetic field. The difference in weight thus obtained is proportional to the gram susceptibility of the complex and the μ_{eff} value was calculated using equation, $\mu_{eff} = 2.828\ [\chi_M{}^{corr}T]^{1/2}$, where $\chi_M{}^{corr} = \chi_M$—Pascal's constant and χ_M = molar susceptibility = gram susceptibility (χ_g) × molecular weight of the sample.

FAB mass spectra

All FAB mass spectra were recorded on a Jeol SX 102/DD 6000 mass spectrometer data system using fast moving Xenon (6 kV, 10 mV) as FAB gas and *m*-nitrobenzyl alcohol as the matrix.

Optical rotation

All specific optical rotations were measured on a Digital Polarimeter Autopol IV, provided with 200 mm sample tube at 21 °C and 589 nm optical wavelength (light source: tungsten–halogen lamp 6 V, 20 W). Solutions of optically pure BINOL (1%) were prepared in THF.

Circular dicroism spectra

All CD spectra were recorded on a Jasco J-810 Spectropolarimeter in the range 250–400 nm, using methanolic solutions of optically active BINOL (0.6 mmol), optically active complexes (0.2 mmol) and methanol as references.

Catalytic reaction analyses

The catalytic reaction products were analyzed, after filtration through Whatman 1.0 μm TF filter by gas chromatography using a Chemito 3865 GC equipped with Oracle software. A 10% SE 30 column (2 M length) packed with 1% QF on chromosorb was used as stationary phase, and ultra pure nitrogen gas with flow rate of 25 ml/min was used as carrier gas. The injection port temperature was kept at 250 °C for complete vaporization of all products. The oven temperature was raised form 80 to 200 °C at a rate of 4 °C/min. The flame ionization detector, kept at 300 °C, was used to detect separated products. A 1 μl sample was injected via syringe for analysis.

The enantiomeric excess (ee) for styrene oxide was determined by GC chiral column GTA (2 M length).

The quantitative analyses were done by external standard method. For that, three different mixtures of standard products were prepared with known concentrations and the response factors were calculated according to percentage area obtained for each of the product with respect to their concentrations. With the help of the response factor, the percentage yields of the products were calculated.

Synthesis of BINOL

BINOL was prepared from β-naphthol as reported earlier,[16,17] giving a racemic mixture of BINOL. To a 1000 ml three-necked round-bottom flask equipped with mechanical stirrer, condenser and dropping funnel was added 14.4 g (0.10 mol) β-naphthol and 600 ml water. The solution was heated to the boiling temperature and then 28 g (0.10 mol) $FeCl_3$ in 60 ml water was added slowly through a dropping funnel. After complete addition, the reaction mixture was boiled for 10 min and the product was filtered, washed with boiling water and dried in air. The crude product was recrystallized from toluene. The purity of the product was checked by TLC, which gave a single spot.

DOI: 10.1002/aoc

Characterization data

M.P.: found 218 °C, reported 218 °C.[16,17] Elemental analyses: found C, 84.0%; H, 4.8%; calculated C, 83.9%; H, 4.9%.

Resolution of racemic BINOL

To obtain enantiopure BINOL, the resolution of racemic BINOL was carried out using (−)-*N*-benzyl cinchonidinium chloride as reported earlier.[18] *R*-(+)-BINOL and *S*-(−)-BINOL obtained with >99% ee were analyzed by melting point, elemental analyses and optical rotation.

Characterization data

R-BINOL: specific rotation, found $[\alpha_D] = +34$ ($c = 1$; THF; 21 °C), Reported $[\alpha_D] = +34$ ($c = 1$; THF; 21 °C).[19] CD, negative cotton effect peak, 273 nm; positive cotton effect peak, 312, 323 and 356 nm (Fig. 1).

S-BINOL: specific rotation, found $[\alpha_D] = -34$ ($c = 1$; THF; 21 °C), reported $[\alpha_D] = -34$ ($c = 1$; THF; 21 °C).[19] CD, positive cotton effect peak, 273 nm; negative cotton effect peak, 312, 323 and 356 nm (Fig. 1).

Synthesis of $[Mn_2^{(III,III)}(BINOL)_3(Bpy)_2]2H_2O$ (complexes 1–3)

To a 50 ml round-bottom flask equipped with magnetic stirring were added 245 mg. (1.00 mmol) of $Mn(OAc)_2{\cdot}2H_2O$ and 429 mg (1.50 mmol) of BINOL [*R*-(+)- or *S*-(−)- or racemic] and 15 ml methanol. The reaction mixture was stirred for 1 h at room temperature. After this time, 156 mg (1.00 mmol) of 2, 2′-bipyridine were added. On stirring for ∼30 min, a yellow colored solid started to precipitate from the solution. The reaction mixture was further stirred for 3 h to allow the reaction to be completed. The solid was filtered, washed with 3 ml methanol and dried *in vacuo* for 3 h.

Characterization data

Complex **1** $[Mn_2^{(III,III)}(R\text{-BINOL})_3(Bpy)_2]2H_2O$: elemental analyses, found C, 73.0%; H, 4.6%; N, 4.4%; calculated C, 73.3%; H, 4.3%; N, 4.3%. CD, negative cotton effect peak, 273 nm; positive cotton effect peak, 312, 323 and 356 nm (Fig. 1). Complex **2** $[Mn_2^{(III,III)}(S\text{-BINOL})_3(Bpy)_2]2H_2O$: elemental analyses, found C, 73.0%; H, 4.5%; N, 4.4%; calculated C, 73.3%; H, 4.3%; N, 4.3%. CD, positive cotton effect peak, 273 nm; negative cotton effect peak, 312, 323 and 356 nm (Fig. 1). Complex **3** $[Mn_2^{(III,III)}(\text{racemic-BINOL})_3(Bpy)_2]2H_2O$: elemental analyses, found C, 73.1%; H, 4.5%; N, 4.3%; calculated C, 73.3%; H, 4.3%; N, 4.3%. FAB mass: $m/z =$ 156, 211, 228, 286, 391, 426, 460, 496, 513, 706, 991, 1310 $\{[Mn_2^{(III,III)}(BINOL)_3(Bpy)_2]2H_2O = 1310$ amu$\}$. Magnetic moment (μ_{eff}): 4.84 BM.

Synthesis of $[Mn_2^{(III,III)}(BINOL)_3(Phen)_2]2H_2O$ (complexes 4–6)

To a 50 ml round-bottom flask equipped with magnetic stirring were added 245 mg (1.00 mmol.) of $Mn(OAc)_2{\cdot}2H_2O$ and 429 mg (1.50 mmol.) of BINOL [*R*-(+)- or *S*-(−)- or racemic] and 15 ml methanol. The reaction mixture was stirred for 1 h at room temperature. After this time, 198 mg (1.00 mmol.) of 1,10-phenanthroline were added. The reaction mixture was further stirred for 1 h at room temperature and then 2 h at below 10 °C. A yellow colored solid formed was filtered, washed with 3 ml of cold methanol and dried *in vacuo* for 3 h.

Characterization data

Complex **4** $[Mn_2^{(III,III)}(R\text{-BINOL})_3(Phen)_2]2H_2O$: elemental analyses, found C, 74.1%; H, 4.3%; N, 4.3%; calculated C, 74.2%; H, 4.1%; N, 4.1%. Complex **5** $[Mn_2^{(III,III)}(S\text{-BINOL})_3(Phen)_2]2H_2O$: elemental

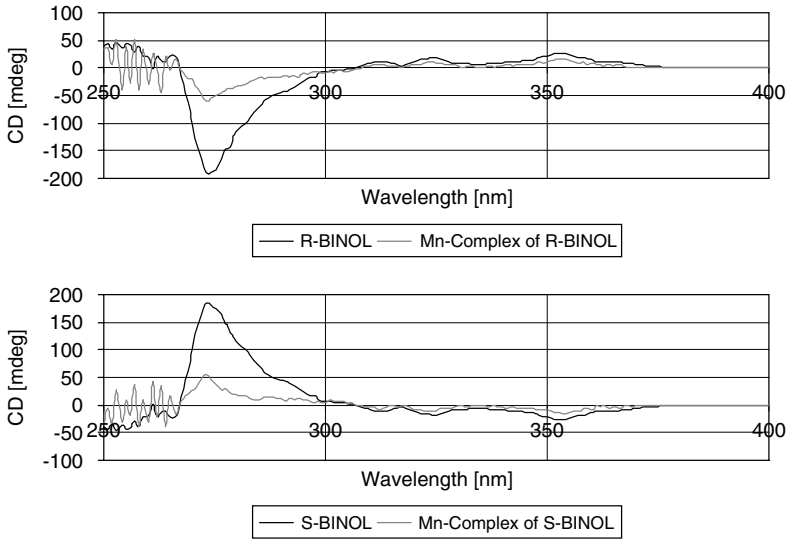


Figure 1. CD Spectra of optically active BINOL and Mn–BINOL complexes.

DOI: 10.1002/aoc

Table 1. Catalytic study of the complexes

Entry	Catalyst	Solvent	Oxidant	Substrate	Time (h)	Conversion (%)	Percentage of yield (percentage of selectivity)		
							Aldehyde	Epoxide	Ketone
1	3	CH_2Cl_2	TBHP	Styrene	24	24	11 (46)	10 (42)	3 (12)
2	6	CH_2Cl_2	TBHP	Styrene	24	19	12 (63)	4 (21)	3 (16)
3	3	CH_3CN	TBHP	Styrene	24	18	10 (55)	5 (28)	3 (17)
4	3	CH_3OH	TBHP	Styrene	24	5	3 (60)	1 (20)	1 (20)
5	3	C_6H_6	TBHP	Styrene	24	11	4 (36)	7 (64)	—
6	3	CH_2Cl_2	PhIO	Styrene	24	5	5 (100)	—	—
7	3	CH_2Cl_2	TBHP	Styrene	1	—	—	—	—
8	3	CH_2Cl_2	TBHP	Styrene	2	—	—	—	—
9	3	CH_2Cl_2	TBHP	Styrene	4	1	1 (100)	—	—
10	3	CH_2Cl_2	TBHP	Styrene	8	5	2.5 (50)	2.5 (50)	—
11	3	CH_2Cl_2	TBHP	Styrene	12	7	3.5 (50)	3.5 (50)	—
12	3	CH_2Cl_2	TBHP	1-hexene	24	<1	—	<1 (100)	—
13	3	CH_2Cl_2	TBHP	1-octene	24	<1	—	<1 (100)	—
14	3	CH_2Cl_2	TBHP	1-decene	24	<1	—	<1 (100)	—

analyses, found C, 74.0%; H, 4.4%; N, 4.3%; Calculated C, 74.2%; H, 4.1%; N, 4.1%. Complex **6** $[Mn_2^{(III,III)}(racemic\text{-}BINOL)_3(Phen)_2]2H_2O$: elemental analyses, found C, 74.0%; H, 4.3%; N, 4.2%; Calculated C, 74.2%; H, 4.1%; N, 4.1%.

Oxidation of olefins

Typical epoxidation reactions were carried out in a dried Schlenk tube, which was washed with acetone and air dried at 100 °C and kept at 30 °C for 1 h before use. The reactions were performed taking substrate (0.50 mmol), oxidant (0.50 mmol) and catalyst (0.005 mmol) in 15 ml solvent. The reaction mixture was stirred at room temperature. The reaction products were analyzed by GC. The catalytic reactions were carried out initially for the complexes **3** and **6** containing racemic BINOL. The reactions were carried out at different parameters like solvent (CH_2Cl_2, CH_3OH, CH_3CN and C_6H_6), oxidant (TBHP, H_2O_2, molecular O_2 and PhIO) and substrate (styrene, 1-hexene, 1-octene and 1-decene) to optimize the reaction condition (Table 1). The optimized conditions were used for further experiments with the optically active BINOL complexes.

RESULTS AND DISCUSSION

Characterization of the complexes

The reaction of $Mn(OAc)_2{\cdot}2H_2O$ with BINOL and N,N′-donor bidentate ligands in methanolic solution at room temperature, resulted in formation of yellow colored mixed ligand binuclear complexes. The mixing in various ratios of metal and ligands (i.e. $Mn(OAc)_2{\cdot}2H_2O$: BINOL : L; 1.00 : 1.50 : 1.00 or 1.00 : 1.00 : 1.00 or 1.00 : 0.50 : 1.00) afforded complexes with same stoichiometry, i.e. $[Mn_2^{(III,III)}(BINOL)_3L_2]2H_2O$. The complexes were characterized by elemental analyses, magnetic susceptibility, IR, electronic, CD and FAB mass spectroscopy.

Elemental analyses

Elemental analyses of complexes correspond to the expected molecular formulae for mixed ligand complexes $[Mn_2^{(III,III)}(BINOL)_3(Bpy)_2]2H_2O$ and $[Mn_2^{(III,III)}(BINOL)_3(Phen)_2]2H_2O$.

Electronic spectra

The electronic spectrum of the complex **3** recorded in CH_2Cl_2, exhibits a peak at ~520 nm. This corresponds to the $^2E \rightarrow {}^2T_2$ d–d transition, indicating a distorted octahedral geometry around a d^4 metal ion.[19]

IR spectra

The IR spectrum of the ligand BINOL shows a band at ~3650–3590 cm^{-1} corresponding to O–H stretching vibrations. The IR spectra of all the complexes show no bands for phenolic O–H groups, indicating coordination of oxygens of the ligand BINOL to the metal ion. The >C═N stretching vibrations of free 2, 2′-bipyridine and 1,10-phenanthroline at ~1660–1640 cm^{-1} were shifted to ~1610–1588 cm^{-1} in all the complexes, indicating coordination of nitrogens of 2, 2′-bipyridine and 1,10-phenanthroline to the metal ion.

Magnetic susceptibility

The magnetic moment ($\mu_{eff} = 4.84$ BM) for complex **3**, corresponds to four unpaired electrons. This indicates the complex to be high spin paramagnetic with $Mn^{(III,III)}$ ions.[20]

DOI: 10.1002/aoc

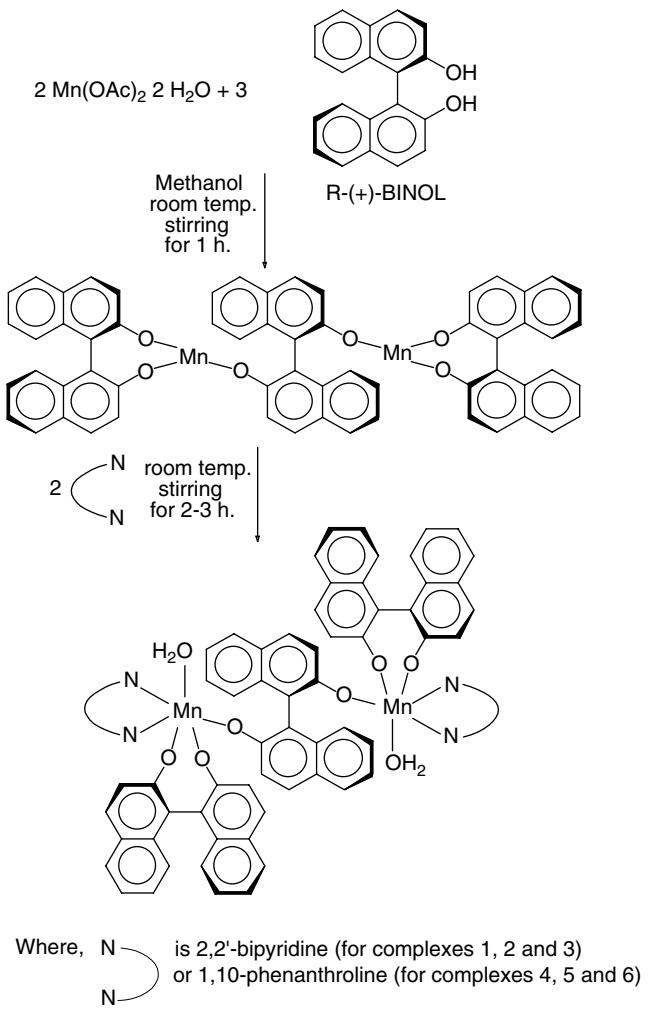
FAB mass spectra

The FAB mass spectral data for complex **3** confirmed formation of the mixed ligand complex. The peak at $m/z = 1310$ corresponds to the parent compound $[Mn_2{}^{(III,III)}(BINOL)_3(Bpy)_2]2H_2O$. Other peaks related to the fragments of the parent compound are also observed and it supports the formation of $[Mn_2{}^{(III,III)}(BINOL)_3(Bpy)_2]2H_2O$ complex.

CD spectra

The CD spectrum (Fig. 1) of complex **1** with *R*-BINOL exhibited a cotton effect opposite to that of the complex **2** with *S*-BINOL. Similar cotton effects were observed in uncoordinated optically active BINOL (*R* and *S*). This observation confirms retention of configuration of BINOL on coordination.

From all the above observations, the probable structure of complexes can be proposed as in Scheme 1.



Scheme 1. Synthesis and probable structure of binuclear $Mn^{(III,III)}$ complexes.

Catalytic study of the complexes

Effect of catalyst

In the initial screening of catalytic activity for oxidation of styrene using catalysts **3** and **6**, it is observed (Table 1, entries 1 and 2) that both gave quite comparable oxidized products. Oxidation of the styrene gave benzaldehyde, styrene oxide and small quantities of acetophenone. Complex **3** was found to be more selective towards epoxide formation, as it gave 10% styrene oxide with 42% chemo-selectivity (Table 1, entry 1).

Effect of solvent

The nature of the solvent has a significant effect on the activity and selectivity of reaction.[21,22] Therefore, the effects of different media, like polar media (e.g. with CH_3OH as solvent), non-polar media (e.g. with CH_2Cl_2 and C_6H_6 as solvents) and coordinating solvent (e.g. CH_3CN) were studied (Table 1, entries 1 and 3–5). In general it is observed that coordinating solvents have greater effects on catalytic activity, which is expected due to their inherent nature of blocking one or more coordination sites.[21,22] However, in the present study, CH_3CN has an adverse effect on epoxidation as more benzaldehyde is formed (10% of yield with 55% chemo-selectivity; Table 1, entry 3). In CH_3OH, the quantities of oxidized products were smaller (4%; Table 1, entry 4), whereas in non-polar solvents like CH_2Cl_2 and C_6H_6, epoxide formed were 10 and 7%, respectively (Table 1, entries 1 and 5). The maximum epoxide formation was found with CH_2Cl_2 (10%; Table 1, entry 1).

Effect of oxidant

Epoxidation of alkenes can be achieved by a variety of oxidants such as the peroxide oxygen donors (e.g. TBHP and H_2O_2), the mono oxygen donor (e.g. PhIO) and dioxygen donor (e.g. molecular O_2).[21,22] When molecular O_2 and H_2O_2 were used as oxidants, the reaction did not proceed at all, and in the case of PhIO, the reaction did not proceed to give desired product epoxide (Table 1, entry 6), whereas, in the case of TBHP, which is a peroxide with a stronger peroxide linkage, the first step involved is formation of metal peroxo complex, followed by M═O species, which is basically the active intermediate in catalytic cycle. Thus, TBHP is the most effective oxidant, as it was found to be more selective towards epoxide formation (Table 1, entry 1).

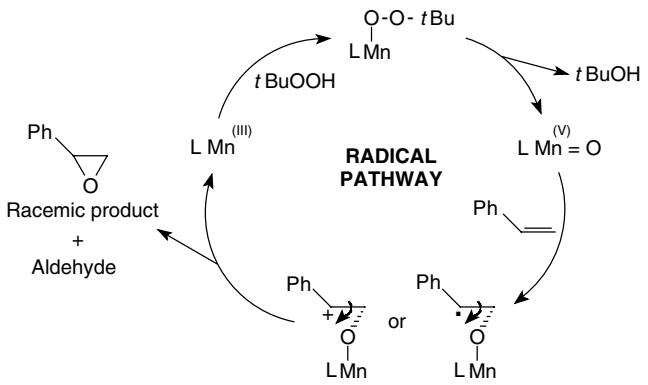
Effect of substrate

The epoxidation reactions were also carried out for different olefins. The different substrates used were styrene, 1-hexene, 1-octene and 1-decene using complex **3** as a representative catalyst. Except for styrene, significant oxidation of the substrate was not observed, as formation of epoxide was found to be less with other substrates (Table 1, entries 1 and 12–14).

Effect of chiral catalyst

As CH_2Cl_2 as a solvent and TBHP as an oxidant were found to be more selective towards epoxide formation, the epoxidation

DOI: 10.1002/aoc



Scheme 2. Proposed mechanism for catalytic epoxidation of styrene.

reactions of styrene were carried out using optically active catalysts (**1** and **2**), to study enantioselectivity of the catalysts, which gave almost negligible enantiomeric excess of the epoxide (<10% ee).

Catalytic mechanism

In order to understand the mechanism[22–25] of the catalytic reaction, electronic spectra of the complexes were recorded before and after addition of TBHP. A band at ~520 nm was observed before addition of TBHP. After addition of TBHP, the solution color changed to dark brown and a new band appeared at ~650 nm. Similar observations have been made in metal catalyzed epoxidation of alkenes[22,23] and formation of $Mn^{(V)} = O$ species as intermediates have been proposed.[22,23] Hence, in the present study the band at ~650 nm suggests formation of $Mn^{(V)} = O$ species (Scheme 2). The new band disappears after 1 h and the color of the solution changes back to original yellow, indicating regeneration of the catalyst.

Kureshy *et al*.[21,22] and Groves *et al*.[24,25] have reported the formation of a carbocation or free radical intermediate to be largely responsible for formation of an aldehyde and racemization of the chiral product. Hence, in the present study, the formation of aldehyde and poor enantioselectivity is observed, probably due to formation of either cationic or radical intermediate or lack of coordination of the substrate during catalytic cycle (Scheme 2).

CONCLUSIONS

The new binuclear $Mn^{(III)}$ complexes of BINOL; $[Mn_2^{(III,III)}(BINOL)_3(Bpy)_2]\,2H_2O$ and $[Mn_2^{(III,III)}(BINOL)_3(Phen)_2]2H_2O$ can be synthesized according to Scheme 1. These complexes were used as catalysts for the epoxidation of olefins and the yields were maximum for complex **3** in CH_2Cl_2 as solvent and TBHP as oxidant. The epoxidation appears to take place via formation of catalytically active $Mn^{(V)} = O$ species. The poor enantioselecivity or racemization of the epoxide and formation of aldehyde may be due to the formation of a cationic or radical intermediate.

Acknowledgements

We are thankful to Dr Rukhsana Kureshy, CSMCRI, Bhavnagar for Chiral GC Analysis. We are also thankful to Professor Shyamal Mazumdar, TIFR, Bombay for recording CD spectra and the Head, CDRI, Lucknow for the FAB mass spectra. Our thanks are due to the Head, Chemistry Department, MSU, Baroda for providing laboratory facilities. One of the authors M.J. Patel, is also thankful to M.S. University for financial support.

REFERENCES

1. Besse P, Veschmbre H. *Tetrahedron* 1994; **50**: 8885.
2. Jacobsen RA, Sharpless KB. *Catalytic Asymmetric Synthesis*, Ojima I (ed.), Chap. 41. VCH: New York, 1993; 103.
3. Jacobsen EN, Pfaltz A, Yamamoto N. *Comprehensive Asymmetric Catalysis*, Vol. II. Springer: Berlin, 1999; 649.
4. Brunel JM. *Chem. Rev.* 2005; **105**: 857.
5. Hashihayata T, Ito Y, Katsuki T. *Tetrahedron* 1997; **53**: 9541.
6. Jacobsen EN, Wu MH. *Comprehensive Asymmetric Catalysis*, Jacobsen EN, Pfaltz A, Yamamoto H (eds), Vol. III. Springer: Berlin, 1999; 1309.
7. Katsuki T. *Catalytic Asymmetric Synthesis*, Ojima I (ed.). Wiley-VCH: New York, 2000; 287.
8. Katsuki T. *J. Mol. Catal. A: Chem.* 1996; **113**: 87.
9. Irie R, Noda K, Ito Y, Matsumoto N, Katsuki T. *Tetrahedron: Asymmetry* 1991; **2**: 481.
10. Marrow JF, Jacobsen EN. *J. Org. Chem.*, 1994; **59**: 1939.
11. Bougauchi M, Watanabe S, Arai T, Sasai H, Shibasaki M. *J. Am. Chem. Soc.*, 1997; **119**: 2329.
12. Kakei H, Nemoto T, Ohshima T, Shibasaki M. *Angew. Chem., Int. Edn* 2004; **43**: 317.
13. Watanabe S, Kobayashi Y, Arai T, Sasai H, Bougauchi M, Shibasaki M. *Tetrahedron Lett.* 1998; **39**: 7353.
14. Nemoto T, Ohshima T, Yamaguchi K, Shibasaki M. *J. Am. Chem. Soc.* 2001; **123**: 2725.
15. Furniss BS, Hannaford AJ, Smith PWG, Tatchell AR. *Vogel's Textbook of Practical Organic Chemistry*, Vogel (ed.), 5th Edn. Longman: Singapore, 1994; 395.
16. Furniss BS, Hannaford AJ, Smith PWG, Tatchell AR. *Vogel's Textbook of Practical Organic Chemistry*, Vogel (ed.), 5th Edn. Longman: Singapore, 1994; 838.
17. Fumio T, Koichi T, Shinji I. *J. Org. Chem.* 1989; **54**(13): 3007.
18. Qiao-Sheng Hu, Dilrukshi V, Lin Pu. *Tetrahedron: Asymmetry* 1995; **6**(9): 2123.
19. Drago RS. *Physical Methods in Chemistry*, Drago RS (ed.), W.B. Saunders: Philadelphia, 1977; 380.
20. Dutta RL, Syamal A. *Elements of Magnetochemistry*, Dutta RL, Syamal A (eds.), 2nd Edn. East-West Press: New Delhi, 1993; 47.
21. Kureshy RI, Khan NH, Abdi SHR, Singh S, Ahmed I, Jasra RV. *J. Mol. Catal. A: Chem.* 2004; **218**: 141.
22. Kureshy RI, Khan NH, Abdi SHR, Singh S, Ahmad I, Jasra RV, Vyas AP. *J. Catal.* 2004; **224**: 229.
23. Srinivasan K, Michaud P, Kochi JK. *J. Am. Chem. Soc.* 1986; **108**: 2309.
24. Groves JT, Nemo TE, Myers RS. *J. Am. Chem. Soc.* 1979; **101**: 1032.
25. Groves JT, Kruper WJ, Nemo TE, Myers RS. *J. Mol. Catal.* 1980; **7**: 169.

DOI: 10.1002/aoc